US009458078B2

(12) **United States Patent**
Liu et al.

(10) **Patent No.: US 9,458,078 B2**
(45) **Date of Patent: Oct. 4, 2016**

(54) **PROCESSES FOR PRODUCING ACETIC ACID FROM A REACTION MEDIUM HAVING LOW ETHYL IODIDE CONTENT**

(71) Applicant: **Celanese International Corporation**, Irving, TX (US)

(72) Inventors: **Yaw-Hwa Liu**, Missouri City, TX (US); **Mark O. Scates**, Houston, TX (US)

(73) Assignee: **CELANESE INTERNATIONAL CORPORATION**, Irvine, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/874,203**

(22) Filed: **Oct. 2, 2015**

(65) **Prior Publication Data**

US 2016/0137575 A1 May 19, 2016

Related U.S. Application Data

(60) Provisional application No. 62/079,979, filed on Nov. 14, 2014.

(51) **Int. Cl.**

C07C 51/12	(2006.01)
C07C 51/44	(2006.01)
C07C 51/48	(2006.01)

(52) **U.S. Cl.**

CPC ***C07C 51/12*** (2013.01); ***C07C 51/44*** (2013.01); ***C07C 51/48*** (2013.01)

(58) **Field of Classification Search**

CPC C07C 51/12; C07C 51/44; C07C 53/08

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,792,620	A	12/1988	Paulik et al.	
5,371,286	A	12/1994	Blay et al.	
5,625,095	A	4/1997	Miura et al.	
5,672,743	A	9/1997	Garland et al.	
5,696,284	A	12/1997	Baker et al.	
5,756,836	A	5/1998	Shimizu et al.	
6,143,930	A *	11/2000	Singh	C07C 51/12 560/232
6,303,813	B1	10/2001	Scates et al.	
6,472,558	B1	10/2002	Key et al.	
6,573,403	B1	6/2003	Joensen	
6,657,078	B2	12/2003	Scates et al.	
6,686,500	B1	2/2004	Watt	
7,223,883	B2	5/2007	Picard et al.	
7,223,886	B2	5/2007	Scates et al.	
7,683,212	B2	3/2010	Kojima et al.	
7,855,306	B2	12/2010	Zinobile et al.	
8,076,507	B2	12/2011	Scates et al.	
8,889,904	B2 *	11/2014	Shaver	C07C 51/44 562/608
8,940,932	B2	1/2015	Shimizu	
8,957,248	B2	2/2015	Miura et al.	
9,006,483	B2	4/2015	Shimizu et al.	
9,073,843	B2	7/2015	Shimizu et al.	
9,115,071	B2	8/2015	Shimizu et al.	
2011/0288333	A1 *	11/2011	Shaver	C07C 51/44 562/608
2013/0264186	A1	10/2013	Shimizu et al.	
2013/0281735	A1	10/2013	Shimizu et al.	

FOREIGN PATENT DOCUMENTS

EP	0 161 874	A1	11/1985
JP	H07-165664	A	6/1995
JP	H10-231267	A	2/1997
JP	2001-181229	A	7/2001
JP	2001-181230	A	7/2001
WO	02/062740	A1	8/2002
WO	2014/115826	A1	7/2014

OTHER PUBLICATIONS

Smith, B.L. et al. (1987). "The Rhodium-Catalyzed Methanol Carbonylation to Acetic Acid at Low Water Concentrations: The Effect of Iodide and Acetate on Catalyst Activity and Stability," *Journal of Molecular Catalysis* 39:115-136.

International Search Report of the corresponding PCT Appln. No. PCT/US2015/053837, dated Feb. 4, 2016.

Office Action received in the corresponding Japanese Patent Application No. 2015-221831, dated Mar. 17, 2016.

* cited by examiner

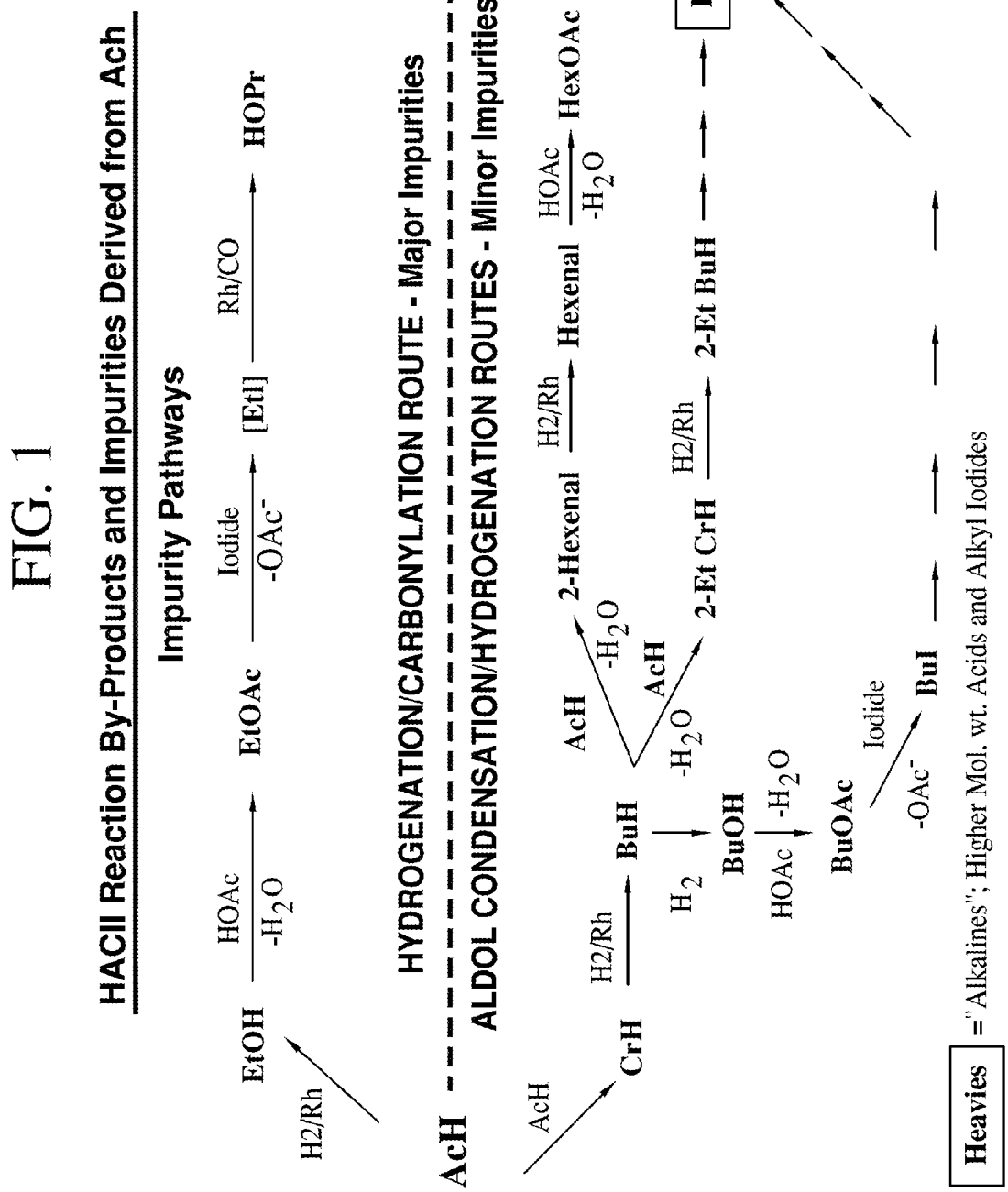
Primary Examiner — Yevegeny Valenrod
Assistant Examiner — Blaine G Doletski
(74) *Attorney, Agent, or Firm* — Kilpatrick Townsend & Stockton LLP

(57) **ABSTRACT**

A process for producing high purity acetic acid from a carbonylation reaction, wherein the carbonylation reaction is carried out while maintaining a low ethyl iodide content in the reaction medium. The ethyl iodide concentration may be maintained by removing acetaldehyde from the reaction medium and/or by adjusting at least one A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium.

26 Claims, 3 Drawing Sheets

FIG. 1


HACII Reaction By-Products and Impurities Derived from Ach
Impurity Pathways
EtOH
EtOAc
HOAc
-H2O
Iodide
-OAc-
[EtI]
Rh/CO
HOPr
H2/Rh
HYDROGENATION/CARBONYLATION ROUTE - Major Impurities
ALDOL CONDENSATION/HYDROGENATION ROUTES - Minor Impurities
AcH
CrH
BuH
BuOH
BuOAc
BuI
AcH
2-Hexenal
-H2O
Hexenal
HexOAc
HexI
2-Et CrH
2-Et BuH
Heavies
H2
HOAc
Iodide
-OAc-
= "Alkalines"; Higher Mol. wt. Acids and Alkyl Iodides

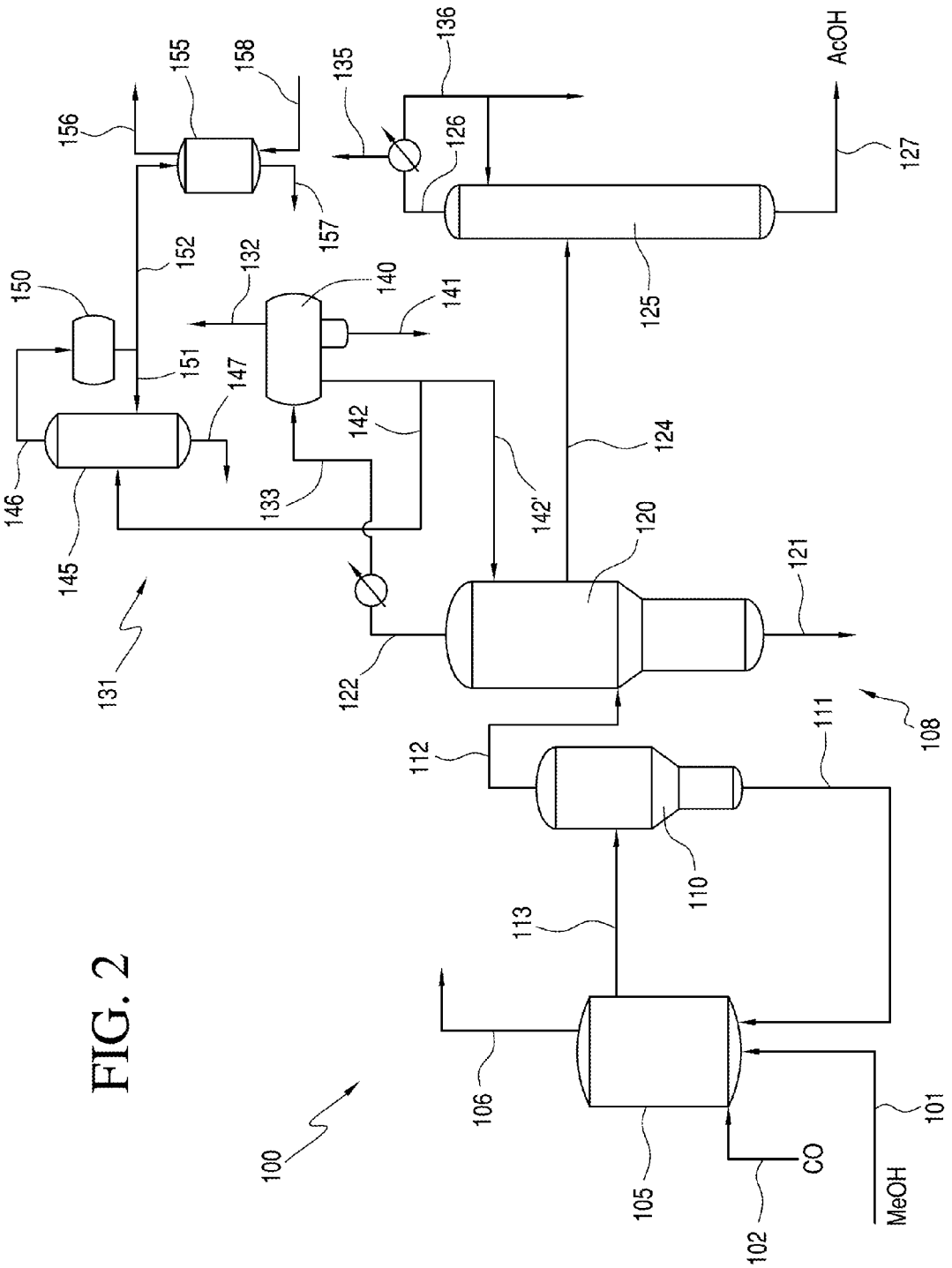
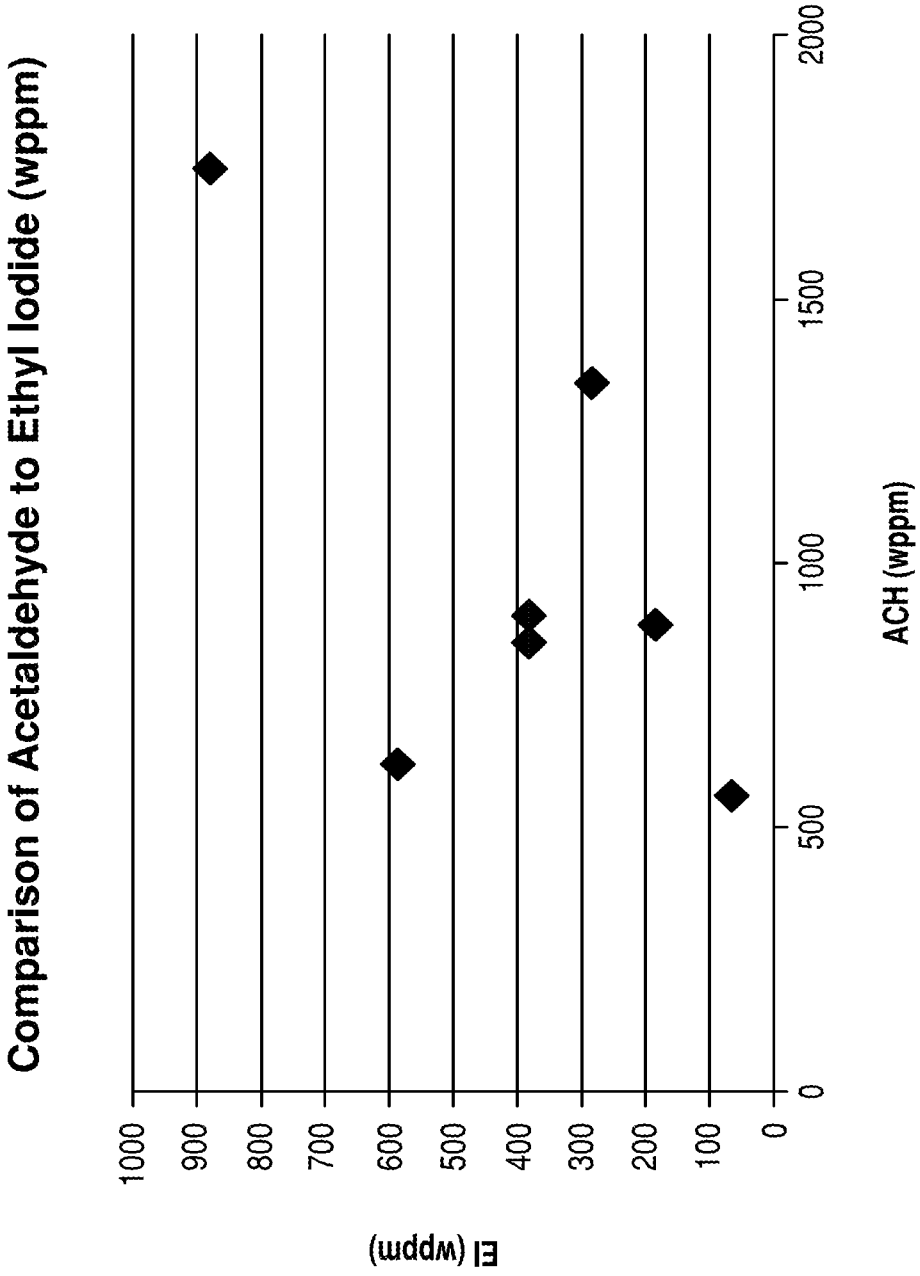

AcOH
MeOH
CO
100
101
102
105
106
108
110
111
112
113
120
121
122
124
125
126
127
131
132
133
135
136
140
141
142
142'
145
146
147
150
151
152
155
156
157
158

FIG. 2

FIG. 3


Comparison of Acetaldehyde to Ethyl Iodide (wppm)
EI (wppm)
1000
900
800
700
600
500
400
300
200
100
0
0
500
1000
1500
2000
ACH (wppm)

PROCESSES FOR PRODUCING ACETIC ACID FROM A REACTION MEDIUM HAVING LOW ETHYL IODIDE CONTENT

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. Provisional Application No. 62/079,979, filed Nov. 14, 2014, the entire content and disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to processes for producing acetic acid and, in particular, to processes for producing acetic acid from a reaction medium having low ethyl iodide content.

BACKGROUND OF THE INVENTION

Among currently employed processes for synthesizing acetic acid, one of the most useful commercially is the catalyzed carbonylation of methanol with carbon monoxide as taught in U.S. Pat. No. 3,769,329, herein incorporated by reference. The carbonylation catalyst contains a metal catalyst, such as rhodium, which is either dissolved or otherwise dispersed in a liquid reaction medium or supported on an inert solid, along with a halogen-containing catalyst promoter as exemplified by methyl iodide. The rhodium can be introduced into the reaction system in many forms. Likewise, because the nature of the halide promoter is not generally critical, a large number of suitable promoters, most of which are organic iodides, may be used. Most typically and usefully, the reaction is conducted by continuously bubbling carbon monoxide gas through a liquid reaction medium in which the catalyst is dissolved.

During the carbonylation of methanol, by-products are formed. These by-products may include alkanes and alkane-like materials. U.S. Pat. No. 5,371,286 teaches a method to improve the quality of certain residues by modifying the separation of alkanes and alkane-like materials and carbonyl-containing impurities from the recycle during the manufacture of acetic acid by the carbonylation of methanol. The improvement in U.S. Pat. No. 5,371,286 comprises operating a prior art stripper column in a reflux manner and partitioning the residue therefrom by the addition of water. The method in U.S. Pat. No. 5,371,286 also reduces the volume of disposal of potentially valuable recyclable reactants. Several steps are claimed in U.S. Pat. No. 5,371,286, including separating a volatile component by causing the volatile component to reflux in a reflux column, removing the volatile portion for further processing, separating a residue into two layers by the addition of water, and recycling an aqueous layer to the reactor. Such a process is referred to herein as an alkane removal system.

An additional by-product formed during the carbonylation of methanol is acetaldehyde. Reduction of acetaldehyde has been described in the art. For example, U.S. Pat. No. 5,756,836 teaches a process for producing a highly purified acetic acid characterized in that the process comprises the step of continuously reacting methanol and/or an aqueous solution of methyl acetate with carbon monoxide in a reactor. A treatment is conducted to limit the concentration of unsaturated compounds in crude acetic acid obtained in the process to 5 wppm or lower, and the resultant crude acetic acid is ozonized. The '836 patent also teaches a process for producing a highly purified acetic acid, characterized by the step of continuously reacting methanol and/or an aqueous solution of methyl acetate with carbon monoxide in a reactor while maintaining the concentration of acetaldehyde in a reaction fluid in the reactor at 1500 wppm or lower. The acetaldehyde concentration is controlled by conducting said reaction at a water content not greater than 10 wt. % and an acetaldehyde concentration of not greater than 1500 wppm to produce a crude acetic acid product mixture; sending the crude acetic acid product mixture to a distillation column to produce a high-boiling point fraction and a low-boiling point fraction; treating the low-boiling point fraction to reduce the content of acetaldehyde therein; and returning the treated low-boiling point fraction to the reaction system.

U.S. Pat. No. 5,625,095 also suggests that acetaldehyde concentration should be reduced. The '095 patent discloses a high purity acetic acid prepared by reacting methanol with carbon monoxide in the presence of a rhodium catalyst, iodide salts, and methyl iodide, wherein an acetaldehyde concentration in the reaction liquid is maintained at 400 wppm or lower. This may be attained by contacting the liquid containing carbonyl impurities with water to separate and remove the carbonyl impurities. After that, the liquid can be returned to the reactor.

U.S. Pat. No. 6,573,403 teaches a process for producing acetic acid which comprises charging reactants methanol, dimethyl ether, methyl acetate or any mixture thereof into a reactor containing: (1) a rhodium carbonylation catalyst, (2) an alkyl iodide or alkyl bromide, and (3) a hydrogenation catalyst, and contacting the reactants with carbon monoxide and hydrogen to produce acetic acid. The '403 patent further teaches that the addition of ruthenium compounds to the carbonylation reaction solution conditions effectively reduces the formation of undesired carbonyl impurities whilst increasing the formation of ethanol, ethyl acetate and ethyl iodide being precursors for the formation of valuable propanoic acid.

Additional methods for removing permanganate reducing compounds (PRC's), including acetaldehyde, are disclosed in U.S. Pat. Nos. 7,855,306 and 7,683,212. The '306 patent teaches a process for reducing and/or removing permanganate reducing compounds or their precursors from intermediate streams during the formation of acetic acid by said carbonylation processes. In particular, a process in which a low boiling overhead vapor stream from a light ends column is subjected to a single distillation to obtain an overhead that is subjected to an extraction to selectively remove and/or reduce PRC's from the process is disclosed. Although alkane removal systems as described herein were able to remove alkanes, they were no longer necessary with the introduction of a permanganate removal system as described in U.S. Pat. No. 7,855,306 since the removal of acetaldehyde reduced the formation of the alkanes. The '212 patent teaches a method to produce acetic acid by continuously reacting methanol with carbon monoxide in the presence of a rhodium catalyst, an iodide salt, methyl iodide, methyl acetate, and water; and thereby producing acetic acid at a production rate of 11 mol/L·hr or more while keeping the acetaldehyde content of a reaction mixture to 500 wppm or less, in which the reaction is carried out at a carbon monoxide partial pressure in a gaseous phase of a reactor of 1.05 MPa or more and/or at a methyl acetate content of the reaction mixture of 2 percent by weight or more to thereby keep the production rate of acetaldehyde to $1/1500$ or less that of acetic acid. The '212 patent teaches that this method can reduce production of by-products without reducing the reac-

tion rate of acetic acid even at a low water content and a low hydrogen partial pressure in a reaction system.

Although the above-described publications focus on suppressing or removing carbonyl impurities such as alkanes, alkane-like materials, and acetaldehyde from carbonylation reaction systems, little art exists concerning the removal or control of the formation of ethyl iodide, which can be formed from these impurities, especially in the absence of an alkane removal process. The need therefore exists for improved processes for producing a reaction medium comprising low amounts of ethyl iodide.

SUMMARY OF THE INVENTION

In one embodiment, the present invention is directed to a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than 250 wppm. The ethyl iodide concentration may range from 1 to 750 wppm. The steps for producing acetic acid product do not comprise an alkane removal system for removing alkanes from the reaction medium. The steps for producing the acetic acid product do not comprise removing propionic acid from and/or reducing propionic concentration in the acetic acid product. The ethyl iodide in the reaction medium and propionic acid in the acetic acid product may be present in a weight ratio from 3:1 to 1:2. The reaction medium may further comprise water in an amount from 0.1 to 14 wt. %. The reactor may be maintained at a temperature from 150 to 250° C. and a total pressure from 25 to 40 atm. The reaction medium may further comprise acetaldehyde in an amount of less than or equal to 150 wppm. The acetaldehyde and ethyl iodide may be present in the reaction medium in a weight ratio from 2:1 to 20:1. The methanol may be introduced into the reactor is a methanol source comprising ethanol in an amount from 1 to 150 wppm. The carbon monoxide may be provided from a carbon monoxide source comprising hydrogen. The ethyl iodide concentration in the reaction medium may be maintained by adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium and/or C) methyl iodide concentration in the reaction medium. The hydrogen partial pressure may be maintained in the reactor at from 0.3 to 2 atm. The methyl acetate concentration of the reaction medium may be maintained at from 0.5 to 30 wt. % or from 1 to 25 wt. %. The ethyl iodide concentration in the reaction medium may be maintained by removing acetaldehyde, comprising: (a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle; (b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde; (c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and (d) extracting a portion of the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide. Methyl iodide from the raffinate may be returned, directly or indirectly, to the reactor. The process may further comprise condensing and biphasically separating the first overhead stream to form a light liquid phase and a heavy phase, wherein at least a portion of the first overhead stream comprises the heavy liquid phase. The process may further comprise condensing and biphasically separating the first overhead stream to form a light liquid phase and a heavy phase, wherein at least a portion of the first overhead stream comprises the heavy liquid phase. The first overhead stream may be phased under conditions sufficient to prevent a phase comprising an emulsion containing ethyl iodide from forming between the light liquid phase and the heavy liquid phase. The heavy liquid phase may comprise ethyl iodide.

In a second embodiment, the present invention is directed to a process for producing acetic acid comprising: providing a reaction medium comprising acetic acid, methanol, methyl acetate, water, a metal catalyst, methyl iodide and a halide organic salt; removing acetaldehyde from a stream derived from the reaction medium to form the acetic acid product; maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium. In some aspects, the ethyl iodide concentration may range from 1 to 750 wppm. The ethyl iodide concentration may also be maintained by adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium and/or C) methyl iodide concentration in the reaction medium. The removing acetaldehyde may comprise: (a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle; (b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde; (c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and (d) extracting the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide. Methyl iodide from the raffinate may be returned, directly or indirectly, to the reactor. The process may further comprise condensing and biphasically separating the first overhead stream to form a light liquid phase and a heavy phase, wherein at least a portion of the light liquid phase may be returned to the reactor. The acetic acid may product may comprise propionic acid in an amount of less than or equal to 250 wppm.

In a third embodiment, the present invention is directed to a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out by adjusting at least one of hydrogen partial pressure, methyl acetate concentration and methyl iodide concentration to maintain ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood in view of the appended non-limiting figures, wherein:

FIG. **1** shows a schematic of acetic acid reaction by-products and impurities derived from acetaldehyde;

FIG. **2** shows a schematic of an acetic acid production process in accordance with the present invention; and

FIG. **3** shows a plot of ethyl iodide concentration versus acetaldehyde concentration in the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. In addition, the processes disclosed herein can also comprise components other than those cited or specifically referred to, as is apparent to one having average or reasonable skill in the art.

In the summary and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, a range "from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific data points, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors possessed knowledge of the entire range and all points within the range.

Throughout the entire specification, including the claims, the following terms have the indicated meanings unless otherwise specified.

As used in the specification and claims, "near" is inclusive of "at." The term "and/or" refers to both the inclusive "and" case and the exclusive "or" case, and is used herein for brevity. For example, a mixture comprising acetic acid and/or methyl acetate may comprise acetic acid alone, methyl acetate alone, or both acetic acid and methyl acetate.

All percentages are expressed as weight percent (wt. %), based on the total weight of the particular stream or composition present, unless otherwise noted. Room temperature is 25° C. and atmospheric pressure is 101.325 kPa unless otherwise noted.

For purposes herein:

acetic acid may be abbreviated as "AcOH";

acetaldehyde may be abbreviated as "AcH";

methyl acetate may be abbreviated "MeAc";

methanol may be abbreviated "MeOH";

methyl iodide may be abbreviated as "MeI";

hydrogen iodide may be abbreviated as "HI";

carbon monoxide may be abbreviated "CO"; and

dimethyl ether may be abbreviated "DME".

HI refers to either molecular hydrogen iodide or dissociated hydroiodic acid when at least partially ionized in a polar medium, typically a medium comprising at least some water. Unless otherwise specified, the two are referred to interchangeably. Unless otherwise specified, HI concentration is determined via acid-base titration using a potentiometric end point. In particular, HI concentration is determined via titration with a standard lithium acetate solution to a potentiometric end point. It is to be understood that for purposes herein, the concentration of HI is not determined by subtracting a concentration of iodide assumed to be associated with a measurement of corrosion metals or other non H+ cations from the total ionic iodide present in a sample.

It is to be understood that HI concentration does not refer to iodide ion concentration. HI concentration specifically refers to HI concentration as determined via potentiometric titration.

This subtraction method is an unreliable and imprecise method to determine relatively lower HI concentrations (e.g., less than about 5 weight percent) due to the fact that it assumes all non-H+ cations (such as cations of Fe, Ni, Cr, Mo) are associated with iodide anion exclusively. In reality, a significant portion of the metal cations in this process can be associated with acetate anion. Additionally, many of these metal cations have multiple valence states, which adds even more unreliability to the assumption on the amount of iodide anion which could be associated with these metals. Ultimately, this method gives rise to an unreliable determination of the actual HI concentration, especially in view of the ability to perform a simple titration directly representative of the HI concentration.

For purposes herein, an "overhead" or "distillate" of a distillation column refers to at least one of the lower boiling condensable fractions which exits at or near the top, (e.g., proximate to the top), of the distillation column, and/or the condensed form of that stream or composition. Obviously, all fractions are ultimately condensable, yet for purposes herein, a condensable fraction is condensable under the conditions present in the process as readily understood by one of skill in the art. Examples of noncondensable fractions may include nitrogen, hydrogen, and the like. Likewise, an overhead stream may be taken just below the upper most exit of a distillation column, for example, wherein the lowest boiling fraction is a non-condensable stream or represents a de-minimis stream, as would be readily understood by one of reasonable skill in the art.

The "bottoms" or "residuum" of a distillation column refers to one or more of the highest boiling fractions which exit at or near the bottom of the distillation column, also referred to herein as flowing from the bottom sump of the column. It is to be understood that a residuum may be taken from just above the very bottom exit of a distillation column, for example, wherein the very bottom fraction produced by the column is a salt, an unusable tar, a solid waste product, or a de-minimis stream as would be readily understood by one of reasonable skill in the art.

For purposes herein, distillation columns comprise a distillation zone and a bottom sump zone. The distillation zone includes everything above the bottom sump zone, i.e., between the bottom sump zone and the top of the column. For purposes herein, the bottom sump zone refers to the lower portion of the distillation column in which a liquid reservoir of the higher boiling components is present (e.g., the bottom of a distillation column) from which the bottom or residuum stream flows upon exiting the column. The bottom sump zone may include reboilers, control equipment, and the like.

It is to be understood that the term "passages," "flow paths," "flow conduits," and the like in relation to internal components of a distillation column are used interchangeably to refer to holes, tubes, channels, slits, drains, and the like, which are disposed through and/or which provide a path for liquid and/or vapor to move from one side of the

internal component to the other side of the internal component. Examples of passages disposed through a structure such as a liquid distributor of a distillation column include drain holes, drain tubes, drain slits, and the like, which allow a liquid to flow through the structure from one side to another.

Average residence time is defined as the sum total of all liquid volume hold-up for a given phase within a distillation zone divided by the average flow rate of that phase through the distillation zone. The hold-up volume for a given phase can include liquid volume contained in the various internal components of the column including collectors, distributors and the like, as well as liquid contained on trays, within downcomers, and/or within structured or random packed bed sections.

Ethyl Iodide Concentrations

The present invention relates to processes for producing acetic acid comprising carbonylating at least one member selected from the group consisting of methanol, dimethyl ether and methyl acetate, in the presence of a water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium. In addition to the carbonylation reaction itself, several additional reactions occur in the reaction medium. Without being bound by theory, FIG. **1** shows various by-products and impurities that may be formed in a carbonylation process by hydrogenation and aldol condensation reactions. When acetaldehyde is present in the reaction medium, it may be hydrogenated to ethanol, which then reacts with acetic acid to form ethyl acetate. The ethyl acetate may then react with an iodide to form ethyl iodide. The ethyl iodide may then react with the metal catalyst and carbon monoxide to form propionic acid. Propionic acid concentration in the acetic acid product may be calculated according to Equation 1.

$$[\text{Propionic Acid (ppm)}] \sim \frac{([EtAc] + [EI])}{([MeAc] + [MeI])} \qquad \text{Equation 1}$$

Thus, although removing acetaldehyde from a stream derived from the reaction medium, which is then recycled to the reaction medium, may indirectly lead to a reduction of ethyl iodide, it is but one of many factors involved in controlling ethyl iodide content. Thus, acetaldehyde removal and methods to achieve this result cannot be directly correlated to ethyl iodide control or reduction. As shown in Equation 1, the concentrations of ethyl acetate, methyl acetate and methyl iodide have an effect on propionic acid concentration. Additionally, ethanol content in the methanol source, hydrogen partial pressure, and hydrogen content in the carbon monoxide source each affect ethyl iodide content and, consequently, propionic acid content in the acetic acid product.

In view of the foregoing, it has now been discovered that acetic acid may be produced by carbonylating at least one member selected from the group consisting of methanol, dimethyl ether and methyl acetate with carbon monoxide in a reactor in the presence of a water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm. The acetic acid is then separated from the reaction medium and the acetic acid product comprises less than or equal to 250 wppm propionic acid. It has been surprisingly and unexpectedly discovered that by controlling the amount of ethyl iodide in the reaction medium, the amount of propionic acid in the acetic acid product can be maintained at less than or equal to 250 wppm.

In embodiments, the concentration of ethyl iodide in the reaction medium is maintained/controlled to be less than or equal to 750 wppm, or e.g., less than or equal to 650 wppm, or less than or equal to 550 wppm, less than or equal to 450 wppm, or less than or equal to 350 wppm. In embodiments, the concentration of ethyl iodide in the reaction medium is maintained/controlled at greater than or equal to 1 wppm, e.g., greater than or equal to 5 wppm, greater than or equal to 10 wppm, greater than or equal to 20 wppm, or greater than or equal to 25 wppm, and less than or equal to 650 wppm, e.g., less than or equal to 550 wppm, less than or equal to 450 wppm, or less than or equal to 350 wppm.

In embodiments, the propionic acid concentration in the acetic acid product is maintained below 250 wppm by maintaining the ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm without removing and/or reducing propionic acid from the acetic acid product. Preferably, the propionic acid concentration in the acetic acid product may be maintained in an amount of less than or equal to 250 wppm, e.g., less than or equal to 225 wppm, less than or equal to 200 wppm, or less than or equal to 150 wppm. By without removing and/or reducing propionic acid from the acetic acid product it is meant that propionic acid is not removed by separation, extraction, adsorption, or reaction outside of the reactor and/or flash vessel. In conventional processes, this propionic acid removal involved a heavy ends column in which the acetic acid product was distilled from the propionic acid and other heavy organic compounds containing carbonyl groups as well as alkyl iodides were separated. Conventionally these heavy ends columns could remove and/or reduce propionic acid from the acetic acid product. Advantageously, by controlling the ethyl iodide concentrations in the reaction medium, the present invention eliminates any need to separately remove and/or reduce propionic acid from the acetic acid product.

Thus, in one embodiment, there is provided a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm, and the propionic acid is not removed and/or reduced from the acetic acid product by distillation, extraction, or adsorption.

Because the processes described herein may include removal of acetaldehyde, a separate alkane removal system is not used. Accordingly, the ethyl iodide concentration of less than or equal to 750 wppm in the reaction medium is not maintained or controlled through alkane removal or through the use of an alkane removal system.

In embodiments, the weight ratio of ethyl iodide in the reaction medium to propionic acid in the acetic acid product may range from 3:1 to 1:2, or e.g., from 5:2 to 1:2, or from 2:1 to 1:2, or from 3:2 to 1:2. In one embodiment, there is provided a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl

iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm and wherein the weight ratio of ethyl iodide in the reaction medium to propionic acid in the acetic acid product may range from 3:1 to 1:2.

In embodiments, the weight ratio of acetaldehyde to ethyl iodide in the reaction medium may range from 20:1 to 2:1, or e.g., from 15:1 to 2:1 or from 9:1 to 2:1. In one embodiment, there is provided a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide, acetaldehyde, and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm, and wherein the weight ratio of acetaldehyde to ethyl iodide in the reaction medium may range from 20:1 to 2:1. In some embodiments the acetaldehyde may be present in the reaction medium in amounts less than or equal to 1500 wppm, e.g., less than or equal to 1200 wppm, less than or equal to 900 wppm, less than or equal to 500 wppm or less than or equal to 400 wppm. In addition to acetaldehyde, there may also be other permanganate reducing compounds ("PRC's"), such as acetone, methyl ethyl ketone, butylaldehyde, crotonaldehyde, 2-ethyl crotonaldehyde, 2-ethyl butyraldehyde, and the aldol condensation products thereof.

In combination with the PRC removal, the ethyl iodide concentration in the reaction medium may be maintained by adjusting at least one of

A) hydrogen partial pressure in the reactor,

B) methyl acetate concentration of the reaction medium; and/or

C) methyl iodide concentration of the reaction medium.

In one embodiment, the ethyl iodide concentration may in the reaction medium may be maintained by maintaining a relatively high hydrogen partial pressure from 0.3 to 2 atm. Although hydrogen partial pressure is not directly measured in the reactor, it can be controlled by the hydrogen introduced to the reactor, reactor vent composition, and production of impurities/byproducts. High hydrogen partial pressure is advantageous for stability of the rhodium catalyst in the reaction medium. The stability of the rhodium catalyst in the reaction medium is difficult to control when hydrogen partial pressure is less than 0.3 atm. To decrease ethyl iodide concentration in the reaction medium, hydrogen partial pressure may be decreased In one embodiment, the ethyl iodide concentration may in the reaction medium may be decreased within the range of 0.3 to 2 atm. For example, if the hydrogen partial pressure is 1.7 atm and the ethyl iodide concentration is 800 ppm, the hydrogen partial pressure may be reduced so long as it is at least 0.3 atm. In another embodiment, the ethyl iodide concentration is maintained by maintaining methyl acetate concentration of the reaction medium from 0.5 to 30 wt. %. In one embodiment, the ethyl iodide concentration may in the reaction medium may be maintained by maintaining methyl iodide concentration of the reaction medium from 1 to 25 wt. %. To decrease ethyl iodide concentration in the reaction medium, methyl acetate concentration in the reaction medium may be reduced. For example, if the methyl acetate concentration is 4 wt. % and the ethyl iodide concentration is 800 ppm, the methyl acetate concentration may be reduced so long as it is at least 0.5 wt. % or 1 wt. %. In another embodiment, the ethyl iodide concentration is maintained by maintaining methyl iodide concentration of the reaction medium from 1 to 25 wt. %. To decrease ethyl iodide concentration in the reaction medium, methyl iodide concentration in the reaction medium may be reduced. For example, when the methyl iodide concentration is 4 wt. % and the ethyl iodide concentration is 800 ppm, the methyl iodide concentration may be reduced so long as it is greater than or equal to 1 wt. %. Thus, in one embodiment, there is provided a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm by adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

Carbonylation Reaction Step

Exemplary reaction and acetic acid recovery system **100** is shown in FIG. **2**. As shown, methanol-containing feed stream **101** and carbon monoxide-containing feed stream **102** are directed to liquid phase carbonylation reactor **105**, in which the carbonylation reaction occurs.

Methanol-containing feed stream **101** may comprise at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate. Methanol-containing feed stream **101** may be derived in part from a fresh feed or may be recycled from the system. At least some of the methanol and/or reactive derivative thereof may be converted to, and hence be present as, methyl acetate in the liquid medium by esterification with acetic acid.

Typical reaction temperatures for carbonylation may be from 150 to 250° C., with the temperature range of 180 to 225° C. being a preferred range. The carbon monoxide partial pressure in the reactor can vary widely but is typically from 2 to 30 atm, e.g., from 3 to 10 atm. The hydrogen partial pressure in the reactor is typically from 0.3 to 2 atm, e.g., from 0.3 to 1.9 atm. In embodiments, the hydrogen partial pressure in the reactor may be greater than or equal to 0.3 atm, e.g., greater than or equal to 0.4 atm, greater than or equal to 0.45 atm, greater than or equal to 0.5 atm, greater than or equal to 0.6 atm, or greater than or equal to 0.7 atm. It is understood at 1 atm is equivalent to approximately 101.33 kPa and 14.70 psi Because of the partial pressure of by-products and the vapor pressure of the contained liquids, the total reactor pressure may range from 15 to 40 atm. The production rate of acetic acid may be from 5 to 50 mol/L·h, e.g., from 10 to 40 mol/L·h, and preferably from 15 to 35 mol/L·h.

Carbonylation reactor **105** is preferably either a mechanically-stirred vessel, a vessel with an educted or pump-around mixing, or a bubble-column type vessel, with or without an agitator, within which the reacting liquid or slurry contents are maintained, preferably automatically, a predetermined level, which preferably remains substantially constant during normal operation. Into carbonylation reactor

105, fresh methanol, carbon monoxide, and sufficient water are continuously introduced as needed to maintain suitable concentrations in the reaction medium.

The metal catalyst may comprise a Group VIII metal. Suitable Group VIII catalysts include rhodium and/or iridium catalysts. When a rhodium catalyst is used, the rhodium catalyst may be added in any suitable form such that rhodium is in the catalyst solution as an equilibrium mixture including $[Rh(CO)_2I_2]$-anion, as is well known in the art. Iodide salts optionally maintained in the reaction mixtures of the processes described herein may be in the form of a soluble salt of an alkali metal or alkaline earth metal, quaternary ammonium, phosphonium salt or mixtures thereof. In certain embodiments, the catalyst co-promoter is lithium iodide, lithium acetate, or mixtures thereof. The catalyst co-promoter may be added as a non-iodide salt that will generate an iodide salt. The catalyst co-promoter may be introduced directly into the reaction system. Alternatively, the iodide salt may be generated in-situ since under the operating conditions of the reaction system, a wide range of non-iodide salt precursors will react with methyl iodide or hydroiodic acid in the reaction medium to generate the corresponding catalyst co-promoter. For additional detail regarding rhodium catalysis and iodide salt generation, see U.S. Pat. Nos. 5,001,259; 5,026,908; 5,144,068 and 7,005,541, which are incorporated herein by reference in their entirety. The carbonylation of methanol utilizing iridium catalyst is well known and is generally described in U.S. Pat. Nos. 5,942,460; 5,932,764; 5,883,295; 5,877,348; 5,877,347; and 5,696,284; which are incorporated herein by reference in their entirety.

The halogen-containing catalyst promoter of the catalyst system consists of a halogen compound comprising an organic halide. Thus, alkyl, aryl, and substituted alkyl or aryl halides can be used. Preferably, the halogen-containing catalyst promoter is present in the form of an alkyl halide. Even more preferably, the halogen-containing catalyst promoter is present in the form of an alkyl halide in which the alkyl radical corresponds to the alkyl radical of the feed alcohol, which is being carbonylated. Thus, in the carbonylation of methanol to acetic acid, the halide promoter may include methyl halide, and more preferably methyl iodide.

The components of the reaction medium are maintained within defined limits to ensure sufficient production of acetic acid. The reaction medium contains a concentration of the metal catalyst, e.g., rhodium catalyst, in an amount from 100 to 3000 wppm, e.g., from 400 to 2000 wppm, or from 400 to 1500 wppm as rhodium. The concentration of water in the reaction medium is maintained to be less than or equal to 14 wt. %, e.g., from 0.1 wt. % to 14 wt. %, from 0.2 wt. % to 10 wt. % or from 0.25 wt. % to 5 wt. %. Preferably, the reaction is conducted under low water conditions and the reaction medium contains water in an amount that is less than or equal to 4.1 wt. %, e.g., less than 3.5 wt. %, less than 3 wt. %, or less than 2 wt. %. In terms of ranges, the reaction medium contains water in an amount from 0.1 to 3.5 wt. %, e.g., from 0.1 to 3 wt. % or from 0.5 to 2.8 wt. %. The concentration of methyl iodide in the reaction medium is maintained to be from 1 to 25 wt. %, e.g., from 5 to 20 wt. %, from 4 to 13.9 wt. %. The concentration of iodide salt, e.g., lithium iodide, in the reaction medium is maintained to be from 1 to 25 wt. %, e.g., from 2 to 20 wt. %, from 3 to 20 wt. %. The concentration of methyl acetate in the reaction medium is maintained to be from 0.5 to 30 wt. %, e.g., from 0.3 to 20 wt. %, from 0.6 to 4.1 wt. %. The concentration of acetic acid in the reaction medium is generally greater than or equal to 30 wt. %, e.g., greater than or equal to 40 wt. % or greater than or equal to 50 wt. %. The above amounts are based on the total weight of the reaction medium.

In embodiments, the process for producing acetic acid further includes introducing a lithium compound into the reactor to maintain the concentration of lithium acetate in an amount from 0.3 to 0.7 wt. % in the reaction medium. In embodiments, an amount of the lithium compound is introduced into the reactor to maintain the concentration of hydrogen iodide in an amount from 0.1 to 1.3 wt. % in the reaction medium. Others have determined hydrogen iodide content indirectly by calculation. U.S. Pub. No. 2013/0310603, for example, indicates that iodide ion concentration may be calculated by subtracting the iodide ion concentration derived from the iodide salt form (including iodides derived from co-catalysts and metal iodide) from the total concentration of iodide ion (I). Such indirect calculation techniques are typically inaccurate, resulting in a poor indication of actual hydrogen iodide concentration owing largely to the inaccuracies of the underlying ion measurement methods. In addition, this indirect calculation technique fails to account for other iodide forms because metal cations are measured and incorrectly assumed to be completely associated only with iodide anions while, in fact, the metal cations may be associated with other anions, such as acetate and catalyst anions. In contrast, the direct measurement of hydrogen iodide concentration as described herein advantageously reflects the actual hydrogen iodide concentration in the system, and can result in accuracy as low as 0.01%.

In embodiments, the concentration of the rhodium catalyst is maintained in an amount from 200 to 3000 wppm in the reaction medium, the concentration of water is maintained in amount from 0.1 to 4.1 wt. % in the reaction medium, and the concentration of methyl acetate is maintained from 0.6 to 4.1 wt. % in the reaction medium, based on the total weight of the reaction medium present within the carbonylation reactor.

In embodiments, the lithium compound introduced into the reactor is selected from the group consisting of lithium acetate, lithium carboxylates, lithium carbonates, lithium hydroxide, other organic lithium salts, and mixtures thereof. In embodiments, the lithium compound is soluble in the reaction medium. In an embodiment, lithium acetate dihydrate may be used as the source of the lithium compound.

Lithium acetate reacts with hydrogen iodide according to the following equilibrium reaction (I) to form lithium iodide and acetic acid:

$$LiOAc+HI \leftrightharpoons LiI+HOAc \quad (I)$$

Lithium acetate is thought to provide improved control of hydrogen iodide concentration relative to other acetates, such as methyl acetate, present in the reaction medium. Without being bound by theory, lithium acetate is a conjugate base of acetic acid and thus reactive toward hydrogen iodide via an acid-base reaction. This property is thought to result in an equilibrium of the reaction (I) which favors reaction products over and above that produced by the corresponding equilibrium of methyl acetate and hydrogen iodide. This improved equilibrium is favored by water concentrations of less than 4.1 wt. % in the reaction medium. In addition, the relatively low volatility of lithium acetate compared to methyl acetate allows the lithium acetate to remain in the reaction medium except for volatility losses and small amounts of entrainment into the vapor crude product. In contrast, the relatively high volatility of methyl acetate allows the material to distill into the purification train, rendering methyl acetate more difficult to control.

Lithium acetate is much easier to maintain and control in the process at consistent low concentrations of hydrogen iodide. Accordingly, a relatively small amount of lithium acetate may be employed relative to the amount of methyl acetate needed to control hydrogen iodide concentrations in the reaction medium. It has further been discovered that lithium acetate is at least three times more effective than methyl acetate in promoting methyl iodide oxidative addition to the rhodium [I] complex.

In embodiments, the concentration of lithium acetate in the reaction medium is maintained at greater than or equal to 0.3 wt. %, greater than or equal to 0.35 wt. %, greater than or equal to 0.4 wt. %, greater than or equal to 0.45 wt. %, or greater than or equal to 0.5 wt. %, and/or in embodiments, the concentration of lithium acetate in the reaction medium is maintained at less than or equal to 0.7 wt. %, less than or equal to 0.65 wt. %, less than or equal to 0.6 wt. %, or less than or equal to 0.55 wt. %.

It has been discovered that an excess of lithium acetate in the reaction medium can adversely affect the other compounds in the reaction medium, leading to decrease productivity. Conversely, it has been discovered that a lithium acetate concentration in the reaction medium below about 0.3 wt. % is unable to maintain the desired hydrogen iodide concentrations in the reaction medium of below 1.3 wt. %.

In embodiments, the lithium compound may be introduced continuously or intermittently into the reaction medium. In embodiments, the lithium compound is introduced during reactor start up. In embodiments, the lithium compound is introduced intermittently to replace entrainment losses.

In some embodiments, the desired reaction rates are obtained even at low water concentrations by maintaining in the reaction medium an ester of the desired carboxylic acid and an alcohol, desirably the alcohol used in the carbonylation, and an additional iodide ion that is over and above the iodide ion that is present as hydrogen iodide. A desired ester is methyl acetate. The additional iodide ion is desirably an iodide salt, with lithium iodide (LiI) being preferred. It has been found, as described in U.S. Pat. No. 5,001,259, that under low water concentrations, methyl acetate and lithium iodide act as rate promoters only when relatively high concentrations of each of these components are present and that the promotion is higher when both of these components are present simultaneously.

The carbonylation reaction of methanol to acetic acid product may be carried out by contacting the methanol feed with gaseous carbon monoxide bubbled through an acetic acid solvent reaction medium containing the rhodium catalyst, methyl iodide promoter, methyl acetate, and additional soluble iodide salt, at conditions of temperature and pressure suitable to form the carbonylation product. It will be generally recognized that it is the concentration of iodide ion in the catalyst system that is important and not the cation associated with the iodide, and that at a given molar concentration of iodide the nature of the cation is not as significant as the effect of the iodide concentration. Any metal iodide salt, or any iodide salt of any organic cation, or other cations such as those based on amine or phosphine compounds (optionally quaternary cations), can be maintained in the reaction medium provided that the salt is sufficiently soluble in the reaction medium to provide the desired level of the iodide. When the iodide is a metal salt, preferably it is an iodide salt of a member of the group consisting of the metals of Group IA and Group IIA of the periodic table as set forth in the "Handbook of Chemistry and Physics" published by CRC Press, Cleveland, Ohio, 2002-03 (83rd edition). In particular, alkali metal iodides are useful, with lithium iodide being particularly suitable. In the low water carbonylation process, the additional iodide ion over and above the iodide ion present as hydrogen iodide is generally present in the catalyst solution in amounts such that the total iodide ion concentration is from 1 to 25 wt. %, the methyl acetate is generally present in amounts from 0.5 to 30 wt. %, and the methyl iodide is generally present in amounts from 1 to 25 wt. %. The rhodium catalyst is generally present in amounts from 200 to 3000 wppm.

In a typical carbonylation process, carbon monoxide is continuously introduced into the carbonylation reactor, desirably below the agitator, which may be used to stir the contents. The gaseous feed preferably is thoroughly dispersed through the reacting liquid by this stirring means. Gaseous purge stream **106** desirably is vented from the reactor **105** to prevent buildup of gaseous by-products and to maintain a set carbon monoxide partial pressure at a given total reactor pressure. In one embodiment, the gaseous purge stream **106** contains low amounts of hydrogen iodide, e.g., less than or equal to 1 wt. %, less than or equal to 0.9 wt. %, less than or equal to 0.8 wt. %, less than or equal to 0.7 wt. %, or less than or equal to 0.5 wt. %. Hydrogen iodide in excess of these amounts may increase the duty on the scrubber to prevent hydrogen iodide from being purged. The temperature of the reactor may be controlled and the carbon monoxide feed is introduced at a rate sufficient to maintain the desired total reactor pressure. Stream **106** comprising the liquid reaction medium exits reactor **105**.

The acetic acid production system preferably includes separation system **108** employed to recover the acetic acid and recycle metal catalyst, methyl iodide, methyl acetate, and other system components within the process. One or more of the recycle streams may be combined prior to being introduced into the reactor. The separation system also preferably controls water and acetic acid content in the carbonylation reactor, as well as throughout the system, and facilitates permanganate reducing compound ("PRC") removal. PRC's may include acetaldehyde, acetone, methyl ethyl ketone, butylaldehyde, crotonaldehyde, 2-ethyl crotonaldehyde, 2-ethyl butyraldehyde, and the aldol condensation products thereof. In one embodiment, a suitable potassium permanganate test is JIS K1351 (2007).

Flash Vessel

The reaction medium is drawn off from the carbonylation reactor **105** at a rate sufficient to maintain a constant level therein and is provided to flash vessel **110** via stream **113**. The flash separation may be carried out at a temperature from 80° C. to 200° C., under an absolute pressure from 1 to 10 atm. In flash vessel **110**, the reaction medium is separated in a flash separation step to obtain a vapor product stream **112** comprising acetic acid and a less volatile catalyst phase as a liquid recycle **111** comprising a catalyst-containing solution.

In addition to acetic acid, vapor product stream **112** also comprises methyl iodide, methyl acetate, water, PRC's. Dissolved gases exiting reactor **105** and entering flash vessel **110** comprise a portion of the carbon monoxide and may also contain gaseous by-products such as methane, hydrogen, and carbon dioxide. Such dissolved gases exit flash vessel **110** as part of the vapor product stream **112**. In one embodiment, carbon monoxide in gaseous purge stream **106** is fed to the base of flash vessel **110** to enhance rhodium stability. The catalyst-containing solution in liquid recycle **111** may be predominantly acetic acid and also contain the rhodium and the iodide salt along with lesser quantities of methyl

acetate, methyl iodide, and water. The catalyst-containing solution in liquid recycle **111** is recycled to the reactor, as discussed above.

In one embodiment, vapor product stream **112** comprises acetic acid, methyl iodide, methyl acetate, water, acetaldehyde, and hydrogen iodide. In one embodiment, vapor product stream **112** comprises acetic acid in an amount from 45 to 75 wt. %, methyl iodide in an amount from 20 to 50 wt. %, methyl acetate in an amount of less than or equal to 9 wt. %, and water in an amount of less than or equal to 15 wt. %, based on the total weight of the vapor product stream. In another embodiment, vapor product stream **112** comprises acetic acid in an amount from 45 to 75 wt. %, methyl iodide in an amount from 24 to less than 36 wt. %, methyl acetate in an amount of less than or equal to 9 wt. %, and water in an amount of less than or equal to 15 wt. %, based on the total weight of the vapor product stream. More preferably, vapor product stream **112** comprises acetic acid in an amount from 55 to 75 wt. %, methyl iodide in an amount from 24 to 35 wt. %, methyl acetate in an amount from 0.5 to 8 wt. %, and water in an amount from 0.5 to 14 wt. %. In yet a further preferred embodiment, vapor product stream **112** comprises acetic acid in an amount from 60 to 70 wt. %, methyl iodide in an amount from 25 to 35 wt. %, methyl acetate in an amount from 0.5 to 6.5 wt. %, and water in an amount from 1 to 8 wt. %. The acetaldehyde concentration in the vapor product stream may be in an amount from 0.005 to 1 wt. %, based on the total weight of the vapor product stream, e.g., from 0.01 to 0.8 wt. %, or from 0.01 to 0.7 wt. %. In some embodiments the acetaldehyde may be present in amounts less than or equal to 0.01 wt. %. Vapor product stream **112** may comprise hydrogen iodide in an amount less than or equal to 1 wt. %, based on the total weight of the vapor product stream, e.g., less than or equal to 0.5 wt. %, or less than or equal to 0.1 wt. %. Vapor product stream **112** is preferably substantially free of, i.e., contains less than or equal to 0.0001 wt. %, propionic acid, based on the total weight of the vapor product stream.

Liquid recycle stream **111** comprises acetic acid, the metal catalyst, corrosion metals, as well as other various compounds. In one embodiment, liquid recycle stream comprises acetic acid in an amount from 60 to 90 wt. %, metal catalyst in an amount from 0.01 to 0.5 wt. %; corrosion metals (e.g., nickel, iron and chromium) in a total amount from 10 to 2500 wppm; lithium iodide in an amount from 5 to 20 wt. %; methyl iodide in an amount from 0.5 to 5 wt. %; methyl acetate in an amount from 0.1 to 5 wt. %; water in an amount from 0.1 to 8 wt. %; acetaldehyde in an amount of less than or equal to 1 wt. % (e.g., from 0.0001 to 1 wt. % acetaldehyde); and hydrogen iodide in an amount of less than or equal to 0.5 wt. % (e.g., from 0.0001 to 0.5 wt. % hydrogen iodide).

Ethyl Iodide Concentration and Control

As described herein, an acetic acid product is desired, preferably an acetic acid product having a propionic acid concentration of less than 250 wppm, e.g., less than 225 wppm or less than 200 wppm. It has now been discovered that the propionic acid concentration of the acetic acid product may be controlled by at least controlling the concentration of ethyl iodide in the reaction medium. It has further been found that the formation of ethyl iodide is effected by numerous variables, including the concentration of acetaldehyde, ethyl acetate, methyl acetate and methyl iodide in the reaction medium. Additionally, ethanol content in the methanol source, hydrogen partial pressure and hydrogen content in the carbon monoxide source each affect ethyl iodide content and, consequently, propionic acid content in the acetic acid product. Further components that may affect ethyl iodide content include catalyst concentration and water concentration in the reaction medium. Surprisingly, control and/or manipulation of these variables, as discussed herein, results in the desired ethyl iodide concentration and, consequently, the desired acetic acid product.

Preferably, the reaction conditions are adjusted to maintain a concentration of ethyl iodide of less than or equal to 750 wppm in the reaction medium, e.g., less than or equal to 650 wppm, less than or equal to 550 wppm, less than or equal to 450 wppm, or less than or equal to 350 wppm. In terms of ranges, the reaction medium may comprise from 1 to 750 wppm ethyl iodide, e.g., from 1 to 700 wppm, from 1 to 600 wppm, from 5 to 650 wppm, from 10 to 550 wppm, from 20 to 450 wppm, or from 25 to 350 wppm. The weight ratio of ethyl iodide in the reaction medium to propionic acid in the acetic acid product may range from 3:1 to 1:2, e.g., from 5:2 to 1:2, from 2:1 to 1:2 or from 3:2 to 1:2.

In one embodiment, the reaction medium comprises the water concentrations, methyl acetate concentrations, methyl iodide concentrations, metal catalyst concentrations, and lithium iodide concentrations disclosed herein. One or more of these concentrations may be adjusted to achieve the desired ethyl iodide concentration, propionic acid concentration, and/or acetaldehyde concentration. Although there may not be a one to one correlation between ethyl iodide concentration in the reaction medium and the adjustment of just one variable, generally, ethyl iodide is controlled by controlling the removal rate of acetaldehyde and by controlling the hydrogen partial pressure. Similarly, reaction temperature and hydrogen concentration in carbon monoxide may be adjusted to maintain an ethyl iodide concentration at less than 750 wppm.

For example, since acetaldehyde content is a factor in determining ethyl iodide and propionic acid concentration, the acetaldehyde concentration in the reaction medium is preferably maintained in an amount of less than or equal to 1500 wppm, e.g., less than or equal to 1200 wppm, less than or equal to 900 wppm, less than or equal to 500 wppm or less than or equal to 400 wppm. Acetaldehyde removal systems suitable for achieving these results are disclosed herein, including in FIG. **2**. The acetaldehyde concentration in the reaction medium may be controlled by removing acetaldehyde from a stream derived from the reaction medium. This includes streams that are intended to be recycled to the reactor and that are derived from the vapor overhead stream, but excludes the acetic acid product stream. The acetaldehyde to ethyl iodide weight ratio in the reaction medium may range from 20:1 to 2:1, e.g., from 15:1 to 2:1 or from 9:1 to 2:1.

As shown in FIG. **1**, the formation or presence of ethanol also affects the concentration of ethyl iodide. At least a portion of the ethanol may be present in the methanol source, which may comprise ethanol in an amount from 1 to 150 wppm, e.g., from 1 to 100 wppm, from 1 to 50 wppm or from 1 to 25 wppm. The ethanol concentration in the methanol source may vary. Optionally, the methanol is purified prior to feeding to the carbonylation reactor. Therefore, the ethanol concentration in the methanol source may be less than 1 wppm, e.g., free of ethanol.

Recovery of Acetic Acid

The distillation and recovery of acetic acid is not particularly limited for the purposes of the present invention. In contrast to previous methods that recover acetic acid from the vapor product stream, the present invention may recover acetic acid from both the vapor product stream and/or a

liquid stream condensed from a portion of the vapor product stream that is enriched in acetic acid.

As shown in FIG. **2**, vapor product stream **112** is directed to a first column **120**, also referred to as a light ends column. Distillation yields a low-boiling overhead vapor stream **122**, a purified acetic acid product that preferably is removed via a side stream **124**, and a high boiling residue stream **121**. In one embodiment, low-boiling overhead vapor stream **122** comprises water in an amount from 40 to 80 wt. %, methyl acetate, methyl iodide, and carbonyl impurities including acetaldehyde. Side stream **124** may comprise acetic acid in an amount from 85 to 98 wt. %, water in an amount from 1 to 5 wt. %, methyl iodide in an amount from 0.1 to 5 wt. %, and methyl acetate in an amount from 0.1 to 5 wt. %. Acetic acid removed via side stream **124** preferably is subjected to further purification, such as in a second column **125**, also referred to as a drying column, and separates side stream **124** to form overhead stream **126** comprised primarily of water and bottoms stream **127** comprised primarily of acetic acid, e.g., the acetic acid product. Propionic acid in column **125** is concentrated with the acetic acid product in an amount of less than 250 wppm and is not removed from the acetic acid product. In some embodiments, the acetic acid product may be taken as a side stream (not shown) from column **125**. Advantageously, this avoids the need for an additional separation step for removing propionic acid from acetic acid. For example, no heavy ends removal is needed.

Overhead stream **126** may comprise water in an amount from 50 to 90 wt. %, e.g., from 50 to 75 wt. %. Methyl acetate and methyl iodide are also removed from the side stream and concentrated in the overhead stream. Drying column bottoms stream **127** preferably comprises acetic acid. In preferred embodiments, drying column bottoms stream **127** comprises acetic acid in an amount greater than 90 wt. %, e.g., greater than 95 wt. % or greater than 98 wt. % and comprises less than 250 wppm propionic acid. Drying column bottoms stream **127** may be further processed, e.g., by passing through an ion exchange resin, prior to being stored or transported for commercial use.

Low-boiling overhead vapor stream **122** separated from first column **120** contains a reaction component, such as methyl iodide, methyl acetate, and water, and it is preferable to retain these reaction components within the process. Low-boiling overhead vapor stream **122** is condensed in a heat exchanger to form stream **133**. At least a portion of stream **133** may be directed to a PRC's removal unit **131**, discussed herein. Optionally, a portion of stream **133** which is recycled to reactor **105** and/or refluxed first column **120**. Similarly, overhead stream **126** from second column **125** contains a reaction component, such as methyl iodide, methyl acetate, and water, and it is preferable to retain these reaction components within the process. Overhead stream **126** is condensed in a heat exchanger to form stream **136**, which is recycled to reactor **105** and/or refluxed second column **125**. An offgas component may be vented via line **135** from condensed low-boiling overhead vapor stream **126**. Similar to the condensed low-boiling overhead vapor stream in stream **133**, condensed overhead stream in stream **136** may also be separated to form an aqueous phase and an organic phase, and these phases may be recycled or refluxed as needed to maintain the concentrations in the reaction medium. In some embodiments, in addition to the condenser, there may be an overhead decanter for collecting the condensed overhead stream **136**. The average residence time of the condensed low-boiling overhead vapor stream **136** in overhead decanter may be greater than or equal to 1 minute, e.g., greater than or equal to 3 minutes, greater than or equal to 5 minutes, or greater than or equal to 10 minutes, and/or the average residence time is less than or equal to 60 minutes, e.g., less than or equal to 45 minutes, less than or equal to 30 minutes, or less than or equal to 25 minutes. High amounts of ethyl iodide in the reaction medium in excess of 750 wppm, which is not removed and then may be carried through the purification process, may cause problems phasing in the decanter by forming a third layer or emulsion between the phases. Because ethyl iodide does not have a means to be removed directly in the process, it is important to prevent a buildup of ethyl iodide in the reaction medium. High amounts of ethyl iodide in the reaction medium can become concentrated to form an undesirable emulsion in the decanter. The emulsion causes poor separation which cannot easily be overcome by increasing the residence time. In some embodiments, the third layer or emulsion may also comprise alkanes. The alkanes, however, are controlled by controlling the acetaldehyde in the reaction medium.

Thus, in one embodiment, there is provided a process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, separating a reaction medium formed in a reactor in a flash vessel to form a liquid recycle and a vapor product stream, distilling the vapor product stream in a first column to obtain a side stream and a low boiling overhead vapor stream, condensing the low boiling overhead vapor stream and biphasically separating the condensed stream to form a heavy liquid phase and a light liquid phase in a decanter under conditions sufficient to prevent an emulsion between the heavy liquid phase and a light liquid phase, and recovering an acetic acid product from the side stream, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

To recover residue liquids from the vent stream, in particular lines **106**, **132**, **135**, and **122**, these lines may be fed to a scrubber that operates with chilled methanol and/or acetic acid to remove methyl acetate and methyl iodide. A suitable scrubber is described in U.S. Pat. No. 8,318,977, which is incorporated herein by reference in its entirety.

The distillation columns of the present invention may be a conventional distillation column, e.g., a plate column, a packed column, and others. Plate columns may include a perforated plate column, bubble-cap column, Kittel tray column, uniflux tray, or a ripple tray column. For a plate column, the theoretical number of plates is not particularly limited and depending on the species of the component to be separate, may include up to 80 plates, e.g., from 2 to 80, from 5 to 60, from 5 to 50, or more preferably from 7 to 35. The distillation column may include a combination of different distillation apparatuses. For example, a combination of bubble-cap column and perforated plate column may be used as well as a combination of perforated plate column and a packed column.

The distillation temperature and pressure in the distillation system can suitably be selected depending on the condition such as the species of the objective carboxylic acid and the species of the distillation column, or the removal target selected from the lower boiling point impurity and the higher boiling point impurity according to the composition of the feed stream. For example, in a case where the purification of acetic acid is carried out by the distillation

column, the inner pressure of the distillation column (usually, the pressure of the column top) may be from 0.01 to 1 MPa, e.g., from 0.02 to 0.7 MPa, and more preferably from 0.05 to 0.5 MPa in terms of gauge pressure. Moreover, the distillation temperature for the distillation column, namely the inner temperature of the column at the temperature of the column top, can be controlled by adjusting the inner pressure of the column, and, for example, may be from 20 to 200° C., e.g., from 50 to 180° C., and more preferably about 100 to 160° C.

The material of each member or unit associated with the distillation system, including the columns, valves, condensers, receivers, pumps, reboilers, and internals, and various lines, each communicating to the distillation system may be made of suitable materials such as glass, metal, ceramic, or combinations thereof, and is not particularly limited to a specific one. According to the present invention, the material of the foregoing distillation system and various lines are a transition metal or a transition-metal-based alloy such as iron alloy, e.g., a stainless steel, nickel or nickel alloy, zirconium or zirconium alloy thereof, titanium or titanium alloy thereof; or aluminum alloy. Suitable iron-based alloys include those containing iron as a main component, e.g., a stainless steel that also comprises chromium, nickel, molybdenum and others. Suitable nickel-based alloys include those containing nickel as a main component and one or more of chromium, iron, cobalt, molybdenum, tungsten, manganese, and others, e.g., HASTELLOY™ and INCONEL™. Corrosion-resistant metals may be particularly suitable as materials for the distillation system and various lines.

PRC Removal System (PRS)

The condensed overhead from the first column, either a portion of light liquid phase and/or heavy liquid phase, when condensed and phased, may be separated and directed to acetaldehyde or PRC removal system to recover methyl iodide and methyl acetate during the acetaldehyde removal process. Without being bound by theory, ethyl iodide tends to concentrate in the heavy liquid phase. Thus, when treating the heavy liquid phase with the PRC removal system, the ethyl iodide may be recycled back to the reactor. Each of the light liquid phase and/or heavy liquid phase contain PRC's in an amount of less than or equal to 1 wt. %, and the process may include removing carbonyl impurities, such as acetaldehyde.

Thus, in one embodiment, there is provided process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, separating stream from a portion the reaction medium enriched in methyl iodide and comprising ethyl iodide and at least one PRC's to remove the at least one PRC from a stream, and recovering an acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

As known in the art, PRC's deteriorate the quality of the acetic acid product and may be removed in suitable impurity removal columns and absorbers as described in U.S. Pat. Nos. 6,143,930; 6,339,171; 7,223,883; 7,223,886; 7,855,306; 7,884,237; 8,889,904; and US Pub. Nos. 2006/0011462, which are incorporated herein by reference in their entirety. Carbonyl impurities, such as acetaldehyde, may react with iodide catalyst promoters to form alkyl iodides, e.g., ethyl iodide, propyl iodide, butyl iodide, pentyl iodide, hexyl iodide, etc. Also, because many impurities originate with acetaldehyde, it is desirable to remove carbonyl impurities from at least one of the liquid light phase and/or heavy liquid phase. As described herein, when a PRC removal system is used, an alkane removal system is not used.

The portion of light liquid phase and/or heavy liquid phase fed to the acetaldehyde or PRC removal system may vary from 1% to 99% of the mass flow of either the light liquid phase **133** and/or heavy liquid phase **134**, e.g., from 1 to 50%, from 2 to 45%, from 5 to 40%, 5 to 30% or 5 to 20%. Also in some embodiments, a portion of both the light liquid phase and heavy liquid phase may be fed to the acetaldehyde or PRC removal system. The portion of the light liquid phase not fed to the acetaldehyde or PRC removal system may be refluxed to the first column or recycled to the reactor, as described herein. The portion of the heavy liquid phase not fed to the acetaldehyde or PRC removal system may be recycled to the reactor. Although a portion of heavy liquid phase may be refluxed to the first column, it is more desirable to return the methyl iodide enriched heavy liquid phase to the reactor.

In one embodiment, a portion of light liquid phase and/or heavy liquid phase is fed to a distillation column which enriches the overhead thereof to have acetaldehyde and methyl iodide. Depending on the configuration, there may be two separate distillation columns, and the overhead of the second column may be enriched in acetaldehyde and methyl iodide. Dimethyl ether, which may be formed in-situ, may also be present in the overhead. The overhead may be subject to one or more extraction stages to remove a raffinate enriched in methyl iodide and an extractant. A portion of the raffinate may be returned to the distillation column, first column, overhead decanter and/or reactor. For example, when the heavy liquid phase is treated in the PRC removal system, it may be desirable to return a portion the raffinate to either the distillation column or reactor. Also, for example, when the light liquid phase is treated in the PRC removal system, it may be desirable to return a portion the raffinate to either the first column, overhead decanter, or reactor. In some embodiments, the extractant may be further distilled to remove water, which is returned to the one or more extraction stages. The column bottoms, which contains more methyl acetate and methyl iodide than light liquid phase, may also be recycled to reactor and/or refluxed to first column.

The PRS may contain a single extraction step or may include multiple extraction stages, as described for example in U.S. Pat. No. 7,223,886 and optionally including multi-stage countercurrent extraction. According to various embodiments, one or more streams derived from either or both (i) the PRS distillation column and/or (ii) the PRS extraction stage, for example, may be returned to the system, e.g., either or both (i) the light ends removal column and/or (ii) the drying column of the separation system for the acetic acid production system. For example, a first portion, e.g., an aliquot portion, of a bottoms stream from a PRS column may be directed to light ends column **120** for further processing, or a second portion, e.g., an aliquot portion, of a bottoms stream from a PRS column may be directed to drying column **125**, preferably the upper portion of drying column **125**, for further processing. As another example, a raffinate from a PRS extraction unit, notably containing methyl iodide, may be returned to the system, e.g., light ends

column or drying column or the raffinate may be added directly to decanter **140** and/or may be returned to reactor **105**.

For purposes of the present specification and claims, the overhead streams and overhead decanters of the light ends removal column and the drying column are considered to be part of the light ends removal column and of the drying column.

As indicated above, either phase of the low-boiling overhead vapor stream **133** may be subsequently processed to remove PRC's.

For purposes of the present specification, it should be understood that the term "aliquot portion" refers to both: (i) a portion of a parent stream that has the same composition as the parent stream from which it is derived, and (ii) a stream comprising a portion of a parent stream that has the same composition as the parent stream from which it is derived and one or more additional streams that have been combined therewith. Thus, directing a return stream comprising an aliquot portion of a PRS distillation bottoms stream to the light ends column encompasses the direct transfer of a portion of the PRS distillation bottoms stream to the light ends column as well as the transfer of a derivative stream comprising (i) a portion of the PRS distillation bottoms stream and (ii) one or more additional streams that are combined therewith prior to introduction into the light ends column. An "aliquot portion" would not include, for example, streams formed in a distillation step or a phase separation step, which would not be compositionally the same as the parent stream from which they are derived nor derived from such a stream.

One of ordinary skill in the art having the benefit of this disclosure can design and operate a PRS distillation column to achieve the desired results. Accordingly, the practice of this process is not necessarily limited to specific characteristic of a particular distillation column or the operation characteristics thereof, such as the total number of stages, the feed point, reflux ratio, feed temperature, reflux temperature, column temperature profile, and the like.

In some cases, it may be advantageous to remove PRCs, primarily aldehydes such as acetaldehyde, from a low-boiling overhead vapor stream of a light ends distillation column, more preferably from the condensed light phase of a low-boiling overhead vapor stream **133** from light ends distillation column **120**.

One or more of the streams from PRS **131** may be returned to the system, e.g., recycled, either directly or indirectly. The PRS preferably includes at least one distillation column and at least one extraction column to reduce and/or remove PRCs. US Patent Publication No. 2011/0288333, which is hereby incorporated by reference, describes various PRS embodiments that may be employed with the present process.

In one embodiment, as shown in FIG. **2**, PRS **131** comprises a column **145**, an accumulator **150**, and an extractor **155**. At least a portion of low-boiling overhead vapor stream **133** is directed to decanter **140** to form a heavy phase stream **141**, and a light phase **142**. Optionally, a portion of stream **142** is returned to column **120** via stream **142'**. Additionally, a portion of heavy phase **141** may be returned to reactor **105**. Optionally, a slip stream (not shown), e.g., from 5 to 40 vol. % or from 5 to 20 vol. % of heavy phase **141** is directed to PRS **131**. An offgas component may be vented via line **132** from decanter **140**. In other embodiments (not shown), a larger portion of heavy phase **141** may be directed to PRS, e.g., from 40 to 100 vol. % heavy phase, from 60 to 100 vol. % or from 80 to 100 vol. %. In these embodiments, light phase **142** may be refluxed to column **120** or optionally, a slip stream of light phase **142** may be directed to the PRS, e.g., from 5 to 40 vol. % or from 5 to 20 vol. %,

At least a portion of light phase **142** is directed to column **145** to form a vapor overhead stream **146** and a bottom process stream **147** comprising water, methyl acetate, methanol, and mixtures thereof. Vapor overhead stream **146** is passed through a condenser and collected in accumulator **150**. A portion of the condensed vapor overhead stream may be returned to column **145** via line **151**. Another portion of the condensed vapor overhead stream is directed to extractor **155** via line **152** to form waste stream **156** comprising at least one PRC, e.g., acetaldehyde, and process stream **157** comprising methyl iodide. An aqueous stream may be provided to extractor **155** via line **158** at a location to obtain a countercurrent flow.

DME may be present in the PRS in amount sufficient to reduce the solubility of methyl iodide in the aqueous extracted phase. Reducing the amount of methyl iodide in the aqueous extracted phase reduces losses of methyl iodide into waste stream **156**. In some embodiments, this may allow multiple extractions as described in U.S. Pat. Nos. 7,223,886, and 8,076,507, the entireties of which are herein incorporated by reference. The amount of DME may vary depending on the methyl iodide concentrations, and in some embodiments, the amount of DME may range from 3 to 9 wt. %, e.g., from 4 to 8 wt. %. DME may be present in the PRS, formed in the PRS by adding water to the PRS (generally by adding water to column **145**) or added to the PRS (generally by adding DME upstream of extractor **155**).

Thus, in one embodiment, there is provided process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, separating a reaction medium formed in a reactor in a flash vessel to form a liquid recycle and a vapor product stream, distilling the vapor product stream in a first column to obtain a side stream and a low boiling overhead vapor stream, condensing the low boiling overhead vapor stream and biphasically separating the condensed stream to form a heavy liquid phase and a light liquid phase, separating a portion of the heavy liquid phase to remove acetaldehyde or other PRC's, and recovering an acetic acid product from the side stream, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

Second Column

Acetic acid removed via side stream **123** preferably is subjected to further purification, such as in a second column **125**, also referred to as a drying column, and separates side stream **123** to form aqueous overhead stream **126** comprised primarily of water and product stream **127** comprised primarily of acetic acid. Water from the side stream is concentrated in the aqueous overhead stream and the aqueous overhead comprises greater than or equal to 90% of the water in the side stream, e.g., greater than or equal to 95%, greater than or equal to 97%, greater than or equal to 99%. Aqueous overhead stream **126** may comprise water in an amount from 50 to 75 wt. %. In embodiments, aqueous overhead stream may comprise water in an amount of less than or equal to 75 wt. %, e.g., less than or equal to 70 wt.

%, less than or equal to 65 wt. %. Methyl acetate and methyl iodide are also removed from the side stream and concentrated in the overhead stream. Product stream **127** preferably comprises or consists essentially of acetic acid and may be withdrawn in the bottom of second column **125** or a side stream near the bottom. When withdrawn as a side stream near the bottom, the side stream may be a liquid or a vapor stream. In preferred embodiments, product stream **127** comprises acetic acid in an amount greater than 90 wt. %, e.g., greater than 95 wt. % or greater than 98 wt. %. Product stream **127** may be further processed, e.g., by passing through an ion exchange resin, prior to being stored or transported for commercial use.

Guard Bed

Carboxylic acid streams, e.g., acetic acid streams, that are contaminated with a halides and/or corrosion metals may be contacted with the ion exchange resin composition under a wide range of operating conditions. Preferably, the ion exchange resin composition is provided in a guard bed. The use of guard beds to purify contaminated carboxylic acid streams is well documented in the art, for example, U.S. Pat. Nos. 4,615,806; 5,653,853; 5,731,252; and 6,225,498, which are hereby incorporated by reference in their entireties. Generally, a contaminated liquid carboxylic acid stream is contacted with the ion exchange resin composition, which is preferably disposed in the guard bed. The halide contaminants, e.g., iodide contaminants, react with the metal to form metal iodides. In some embodiments, hydrocarbon moieties, e.g., methyl groups, that may be associated with the iodide may esterify the carboxylic acid. For example, in the case of acetic acid contaminated with methyl iodide, methyl acetate would be produced as a byproduct of the iodide removal. The formation of this esterification product typically does not have a deleterious effect on the treated carboxylic acid stream.

In one embodiment, the ion exchange resin is a metal-exchanged ion exchange resin and may comprise at least one metal selected from the group consisting of silver, mercury, palladium and rhodium. In one embodiment, at least 1% of the strong acid exchange sites of said metal-exchanged resin are occupied by silver. In another embodiment, at least 1% of the strong acid exchange sites of said metal-exchanged resin are occupied by mercury. The process may further comprise treating the purified acetic acid product with a cationic exchange resin to recover any silver, mercury, palladium or rhodium.

The pressure during the contacting step is limited only by the physical strength of the resin. In one embodiment, the contacting is conducted at pressures ranging from 0.1 MPa to 1 MPa, e.g., from 0.1 MPa to 0.8 MPa or from 0.1 MPa to 0.5 MPa. For convenience, however, both pressure and temperature preferably may be established so that the contaminated carboxylic acid stream is processed as a liquid. Thus, for example, when operating at atmospheric pressure, which is generally preferred based on economic considerations, the temperature may range from 17° C. (the freezing point of acetic acid) to 118° C. (the boiling point of acetic acid). It is within the purview of those skilled in the art to determine analogous ranges for product streams comprising other carboxylic acid compounds. The temperature of the contacting step preferably is kept relatively low to minimize resin degradation. In one embodiment, the contacting is conducted at a temperature ranging from 25° C. to 120° C., e.g., from 25° C. to 100° C. or from 50° C. to 100° C. Some cationic macroreticular resins typically begin degrading (via the mechanism of acid-catalyzed aromatic desulfonation) at temperatures of 150° C. Carboxylic acids having up to 5 carbon atoms, e.g., up to 3 carbon atoms, remain liquid at these temperatures. Thus, the temperature during the contacting should be maintained below the degradation temperature of the resin utilized. In some embodiments, the operating temperature is kept below temperature limit of the resin, consistent with liquid phase operation and the desired kinetics for halide removal.

The configuration of the guard bed within an acetic acid purification train may vary widely. For example, the guard bed may be configured after a drying column. Additionally or alternatively, the guard be may be configured after a heavy ends removal column or finishing column. Preferably the guard bed is configured in a position wherein the temperature acetic acid product stream is low, e.g., less than 120° C. or less than 100° C. Aside from the advantages discussed above, lower temperature operation provides for less corrosion as compared to higher temperature operation. Lower temperature operation provides for less formation of corrosion metal contaminants, which, as discussed above, may decrease overall resin life. Also, because lower operating temperatures result in less corrosion, vessels advantageously need not be made from expensive corrosion-resistant metals, and lower grade metals, e.g., standard stainless steel, may be used.

In one embodiment, the flow rate through the guard bed ranges from 0.1 bed volumes per hour ("BV/hr") to 50 BV/hr, e.g., 1 BV/hr to 20 BV/hr or from 6 BV/hr to 10 BV/hr. A bed volume of organic medium is a volume of the medium equal to the volume occupied by the resin bed. A flow rate of 1 BV/hr means that a quantity of organic liquid equal to the volume occupied by the resin bed passes through the resin bed in a one hour time period.

To avoid exhausting the resin with a purified acetic acid product that is high in total iodide concentration, in one embodiment the purified acetic acid product in bottoms stream **127** is contacted with a guard bed when total iodide concentration of the purified acetic acid product is less than 5 wppm, e.g., preferably less than 1 wppm. Total iodide concentration includes iodide from both organic, C_1 to C_{14} alkyl iodides, and inorganic sources, such as hydrogen iodide. However, for purposes of the present invention ethyl iodide generally is not removed by guard beds. Instead methyl iodide and higher alkyl iodides, C_6 to C_{14} alkyl iodides. A purified acetic acid composition is obtained as a result of the guard bed treatment. The purified acetic acid composition, in one embodiment, comprises less than 100 wppb iodides, e.g., less than 90 wppb, less than 50 wppb, or less than 25 wppb. In one embodiment, the purified acetic acid composition comprises less than 1000 wppb corrosion metals, e.g., less than 750 wppb, less than 500 wppb, or less than 250 wppb. For purposes of the present invention, corrosion metals include metals selected from the group consisting of nickel, iron, chromium, molybdenum and combinations thereof. In terms of ranges, the purified acetic acid composition may comprise from 0 to 100 wppb iodides, e.g., from 1 to 50 wppb; and/or from 0 to 1000 wppb corrosion metals, e.g., from 1 to 500 wppb. In other embodiments, the guard bed removes at least 25 wt. % of the iodides from the crude acetic acid product, e.g., at least 50 wt. % or at least 75 wt. %. In one embodiment, the guard bed removes at least 25 wt. % of the corrosion metals from the crude acetic acid product, e.g., at least 50 wt. % or at least 75 wt. %.

As is evident from the figures and text presented above, a variety of embodiments are contemplated.

E1. A process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal

catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

E2. The process according to embodiment E1, wherein the steps do not comprise removing propionic acid from and/or reducing propionic acid concentration in the acetic acid product.

E3. The process according to embodiment E1 or E2, wherein the steps do not comprise an alkane removal system for removing alkanes from the reaction medium.

E4. The process according to any one of embodiments E1 to E3, wherein the ethyl iodide concentration in the reaction medium is from 1 to 750 wppm.

E5. The process according to any one of embodiments E1 to E4, wherein ethyl iodide in the reaction medium and propionic acid in the acetic acid product are present in a weight ratio from 3:1 to 1:2.

E6. The process according to any one of embodiments E1 to E5, wherein the reaction medium comprises water in an amount from 0.1 to 14 wt. %.

E7. The process according to any one of embodiments E1 to E6, wherein the reactor is maintained at a temperature from 150 to 250° C. and a total pressure from 25 to 40 atm.

E8. The process according to any one of embodiments E1 to E7, wherein the reaction medium further comprises acetaldehyde in an amount of less than or equal to 1500 wppm.

E9. The process according to any one of embodiments E1 to E8, wherein acetaldehyde and ethyl iodide are present in the reaction medium in a weight ratio from 2:1 to 20:1.

E10. The process according to any one of embodiments E1 to E9, wherein the methanol is introduced into the reactor is a methanol source comprising ethanol in an amount from 1 to 150 wppm.

E11. The process according to any one of embodiments E1 to E10, wherein the ethyl iodide concentration in the reaction medium is maintained by:

adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium, and

separating the acetic acid product from the reaction medium.

E12. The process according to embodiment E11, wherein the hydrogen partial pressure is maintained in the reactor from 0.3 to 2 atm.

E13. The process according to embodiment E11, wherein the methyl acetate concentration of the reaction medium is maintained from 0.5 to 30 wt. %.

E14. The process according to embodiment E11, wherein the methyl acetate concentration of the reaction medium is maintained from 1 to 25 wt. %.

E15. The process according to any one of embodiments E1 to E10, wherein the ethyl iodide concentration is maintained in the reaction medium by removing acetaldehyde from a stream derived from the reaction medium.

E16. The process according to embodiment E15, wherein the ethyl iodide concentration is maintained by removing acetaldehyde using a process comprising:

(a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle;

(b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde;

(c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and

(d) extracting a portion of the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide.

E17. The process according to embodiment E16, wherein the methyl iodide from the raffinate is returned, directly or indirectly, to the reactor.

E18. The process according to embodiment E17, further comprising condensing and biphasically separating the first overhead stream to form a light liquid phase and a heavy liquid phase, wherein the at least a portion of the first overhead stream distilled in step (c) comprises the heavy liquid phase.

E19. The process according to embodiment E18, wherein the first overhead stream is phased under conditions sufficient to prevent a phase comprising an emulsion containing ethyl iodide from forming between the light liquid phase and the heavy liquid phase.

E20. The process according to embodiment E18, wherein the heavy liquid phase comprises ethyl iodide.

E21. A process for producing an acetic acid product, comprising:

providing a reaction medium comprising acetic acid, methanol, methyl acetate, water, a metal catalyst, methyl iodide and a halide organic salt;

removing acetaldehyde from a stream derived from the reaction medium;

maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm; and

separating the acetic acid product from the reaction medium.

E22. The process according to embodiment E21, wherein the ethyl iodide concentration in the reaction medium is from 1 to 750 wppm.

E23. The process according to embodiment E21, wherein the stream derived from the reaction medium is enriched in methyl iodide.

E24. The process according to embodiment E21, wherein the removing acetaldehyde further comprises:

(a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle;

(b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde;

(c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and

(d) extracting the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide.

E25. The process according to embodiment E21, wherein the methyl iodide from the raffinate is returned, directly or indirectly, to the reactor.

E26. The process according to embodiment E21, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

E27. A process for producing an acetic acid product, comprising the steps of continuously carbonylating at least one member selected from the group consisting of methanol, dimethyl ether, and methyl acetate with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out by adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium, and separating the acetic acid product from the reaction medium to maintain ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium.

While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited below and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

EXAMPLES

The present invention will be better understood in view of the following non-limiting examples.

Example 1

Samples A-C

Carbon monoxide and methanol, a rhodium catalyst mixture comprising a rhodium catalyst, methyl iodide, lithium iodide and methyl acetate were fed to a microunit. The methanol contained from 5 to 15 wppm ethanol. The temperature was kept constant as was the reaction pressure, while other conditions and components were varied. The concentrations of acetaldehyde and ethyl iodide were measured and are reported in Table 1 below.

Example 2

Sample D-F

Carbon monoxide, methanol, a rhodium catalyst mixture comprising a rhodium catalyst, methyl iodide, lithium iodide and methyl acetate were fed to a pilot plant. The temperature was kept essentially constant (within 2° C. between all examples) while other conditions and components were varied. The concentrations of acetaldehyde and ethyl iodide were measured and are reported in Table 1 below. Example F is a comparative example while Samples A-E are inventive.

TABLE 1

Acetaldehyde and Ethyl Iodide Concentration in Reaction Mixture

Sample	Temp. (° C.)	Pressure (atm)	H_2 partial pressure (atm)	MeI (wt. %)	MeOAc (wt. %)	H_2 in CO (mol. %)	AcH (wppm)	EI (wppm)	AcH:EI weight ratio
A	195	28	0.27	11.2	2.9	0.005	560	64	8.75
B	195	28	0.35	11.4	2.5	0.19	880	185	4.76
C	195	28	0.5	11.3	2.8	0.28	1342	283	4.74
D	196	26	0.27	11.8	3.2	0.19	900	380	2.37
E	196	28.5	0.35	12.5	3	0.06	850	380	2.24
F	198	27	0.40	11.4	2.6	0.11	1750	879	1.99

As shown in Table 1 and as plotted in FIG. **3**, Samples A-F indicate that the relationship between acetaldehyde concentration and ethyl iodide concentration is highly inconsistent and unpredictable. By comparing Samples A to C, performed in the microunit, the trend between increased ethyl iodide with increased acetaldehyde, increased hydrogen partial pressure and hydrogen in carbon monoxide is apparent. This trend is also seen by comparing Sample D to F, performed in a pilot plant.

Example 3

The reaction mixture of each of Samples A-F was removed from the reactor and passed through a flash vessel, light ends column and drying column as described in FIG. **2**. No heavy ends removal of the propionic acid, or of any components having a higher boiler point than acetic acid, was performed. The propionic acid concentration in the acetic acid product was measured. The results are shown in Table 2 below, in comparison to the acetaldehyde concentration and ethyl iodide concentration in the reaction mixture.

TABLE 2

Propionic Acid Concentration in Acetic Acid Product

Sample	AcH (wppm)	EI (wppm)	HOPr (wppm)	EI:HOPr weight ratio
A	560	64	117	0.55
B	880	185	159	1.16
C	1342	283	250	1.13
D	900	380	260	1.46
E	850	380	236	1.61
F	1750	879	327	2.7

As shown in Table 2, when ethyl iodide content is less than 750 wppm and acetaldehyde concentration is less than

1500 wppm, propionic acid concentration in the acetic acid product is less than 250 wppm.

We claim:

1. A process for producing an acetic acid product, comprising the steps of continuously carbonylating methanol with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out while maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm,

wherein the methanol that is introduced into the reactor is a methanol source comprising ethanol in an amount from 1 to 150 wppm.

2. The process of claim **1**, wherein the steps do not comprise removing propionic acid from and/or reducing propionic acid concentration in the acetic acid product.

3. The process of claim **1**, wherein the steps do not comprise an alkane removal system for removing alkanes from the reaction medium.

4. The process of claim **1**, wherein the ethyl iodide concentration in the reaction medium is from 1 to 750 wppm.

5. The process of claim **1**, wherein ethyl iodide in the reaction medium and propionic acid in the acetic acid product are present in a weight ratio from 3:1 to 1:2.

6. The process of claim **1**, wherein the reaction medium comprises water in an amount from 0.1 to 14 wt. %.

7. The process of claim **1**, wherein the reactor is maintained at a temperature from 150 to 250° C. and a total pressure from 25 to 40 atm.

8. The process of claim **1**, wherein the reaction medium further comprises acetaldehyde in an amount of less than or equal to 1500 wppm.

9. The process of claim **8**, wherein acetaldehyde and ethyl iodide are present in the reaction medium in a weight ratio from 2:1 to 20:1.

10. The process of claim **1**, wherein the ethyl iodide concentration in the reaction medium is maintained by:

adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium, and

separating the acetic acid product from the reaction medium.

11. The process of claim **10**, wherein the hydrogen partial pressure is maintained in the reactor from 0.3 to 2 atm.

12. The process of claim **10**, wherein the methyl acetate concentration of the reaction medium is maintained from 0.5 to 30 wt. %.

13. The process of claim **10**, wherein the methyl acetate concentration of the reaction medium is maintained from 1 to 25 wt. %.

14. The process of claim **1**, wherein the ethyl iodide concentration is maintained in the reaction medium by removing acetaldehyde from a stream derived from the reaction medium.

15. The process of claim **14**, wherein the ethyl iodide concentration is maintained by removing acetaldehyde using a process comprising:

(a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle;

(b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde;

(c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and

(d) extracting a portion of the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide.

16. The process of claim **15**, wherein the methyl iodide from the raffinate is returned, directly or indirectly, to the reactor.

17. The process of claim **16**, further comprising condensing and biphasically separating the first overhead stream to form a light liquid phase and a heavy liquid phase, wherein the at least a portion of the first overhead stream distilled in step (c) comprises the heavy liquid phase.

18. The process of claim **17**, wherein the first overhead stream is phased under conditions sufficient to prevent a phase comprising an emulsion containing ethyl iodide from forming between the light liquid phase and the heavy liquid phase.

19. The process of claim **17**, wherein the heavy liquid phase comprises ethyl iodide.

20. A process for producing an acetic acid product, comprising:

providing a reaction medium comprising acetic acid, methanol, water, a metal catalyst, methyl iodide and a halide organic salt;

removing acetaldehyde from a stream derived from the reaction medium;

maintaining an ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm; and

separating the acetic acid product from the reaction medium

wherein the methanol that is introduced into the reaction medium is a methanol source comprising ethanol in an amount from 1 to 150 wppm.

21. The process of claim **20**, wherein the ethyl iodide concentration in the reaction medium is from 1 to 750 wppm.

22. The process of claim **20**, wherein the stream derived from the reaction medium is enriched in methyl iodide.

23. The process of claim **20**, wherein the removing acetaldehyde further comprises:

(a) separating at least a portion of the reaction medium to provide a vapor overhead stream comprising acetic acid and a liquid recycle;

(b) distilling the vapor overhead stream to yield a purified acetic acid product and a first overhead stream comprising methyl iodide, water, acetic acid, methyl acetate, and acetaldehyde;

(c) distilling at least a portion of the first overhead stream to form a second overhead stream and a liquid phase residuum, wherein the second overhead stream is enriched with acetaldehyde with respect to the at least a portion of the first overhead stream; and

(d) extracting the second overhead stream with water to obtain an aqueous acetaldehyde stream comprising acetaldehyde and a raffinate comprising methyl iodide.

24. The process of claim **23**, wherein the methyl iodide from the raffinate is returned, directly or indirectly, to the reactor.

25. The process of claim 20, wherein the acetic acid product comprises propionic acid in an amount of less than or equal to 250 wppm.

26. A process for producing an acetic acid product, comprising the steps of continuously carbonylating methanol with carbon monoxide in a reactor in the presence of water, a metal catalyst, methyl iodide and a halide salt to form a reaction medium, wherein the carbonylating is carried out by adjusting at least one of A) hydrogen partial pressure in the reactor, B) methyl acetate concentration of the reaction medium; and/or C) methyl iodide concentration of the reaction medium, and separating the acetic acid product from the reaction medium to maintain ethyl iodide concentration in the reaction medium at less than or equal to 750 wppm, and separating the acetic acid product from the reaction medium, wherein the methanol that is introduced into the reactor is a methanol source comprising ethanol in an amount from 1 to 150 wppm.

* * * * *